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13. ABSTRACT (Maximum 200 words) Using state-of-the-art theoretical techniques, we have studied the role that the size, symmetry and composition play on the electronic properties of finite metallic systems. The work focussed on studying the dissociative chemisorption of hydrogen on cluster surfaces, pairing of hydrogen in transition and rare-earth metals and the effect of symmetry and topology on magnetism in clusters. The systems studied include magnetism of transition metal clusters and quasi-crystals, geometry and electronic structure of metal-carbon complexes, optical properties of compound metal clusters, and hydrogen uptake of neutral and charged metal clusters. Clusters as a building block of a new class of materials and properties of cluster assemblies were also investigated. The studies elucidated the novel physics and chemistry of systems with reduced size, symmetry, and dimensions. The work may lead to technological developments of clusters as a new source of atomically engineered materials.				
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This is the final report on our Army office research grant on " Electronic Structure of Finite Systems ". We have had a very productive period during the three year cycle that began in February, 1992. We have published/submitted 53 papers and books, of which 35 papers carry exclusive citation to the Army contract. Many of these papers have appeared in rapid communication journals, such as the Physical Review Letters, Chemical Physical Letters, Science, etc. Our work has also been featured in popular magazines and newspapers.¹ We were invited to give talks at 27 international conferences and 26 seminars/colloquia worldwide. We have organized 7 conferences/workshops including symposia and focussed sessions for the American Physical Society and the Gordon Research Conference. Three students have graduated with either M.S. or Ph.D, or both degrees. In the following, we present (A) the highlights of research completed thus far, (B) the resulting publications, (C) professional activities, including organization of conferences and workshops and invitations to speak at scientific meetings, (D) degrees earned by students, and (E) personnel supported.

A. Research Highlights

During the past two and one-half years, we have concentrated on electronic structure, stability, and properties of a variety of metal clusters. It is difficult to describe, even briefly, all the work we have done as we published/submitted 36 papers during this period under the Army funding alone. In the following, we provide only briefly an outline of the salient features of our work and refer the reader to the papers at the end of this report for details.

(i) Magnetism of Finite Systems

Although the ground states of most atoms are magnetic, very few of them order magnetically in the bulk. A number of factors, such as interatomic spacing, local symmetry, and coordination numbers are responsible for this phenomenon.² How various factors control magnetic ordering can be best understood by studying atomic clusters. As clusters grow, their surface-to-volume ratio, symmetry, topology, and local coordination undergo continuous changes. We expended considerable effort³⁻¹¹ to understand the fundamental mechanisms that underlie the magnetism of clusters, surfaces, and quasicrystals. We were not only able to explain⁵ recent experiments that had apparent contradictions with long-standing theoretical predictions, but also were able to predict⁹ new magnetic clusters that prompted new experimental investigations¹² eventually leading to the confirmation of our theory.

An analysis² of voluminous data on the magnetic moments of 3d transition metal atoms confined to linear chains, surfaces, and

thin films suggests that magnetic moments decrease as coordination numbers increase. This means that atoms in clusters will be more magnetic than those in bulk and that the average moment of a cluster should decrease as clusters grow in size. The experiments on Fe, Co, and Ni clusters just proved to the contrary. We provided the first theoretical explanation¹³ that this apparent contradiction was due to the supermagnetic nature of clusters. Here all the atomic moments in a cluster are aligned ferromagnetically, but the cluster moment undergoes fluctuations in direction due to thermal energy. This explanation accounts for most of the experimental observation¹⁴ and has become a standard interpretation of cluster magnetism.

We also investigated the magnetism of 4d transition metal clusters.⁹ Unlike the 3d transition metals, the 4d transition metals are not magnetic in the bulk state. Yet magnetism can be induced in them with proper doping. For example, Fe impurities induce giant magnetic moments in Pd.¹⁵ We studied⁹ clusters consisting of Pd, Rh, and Ru to see if reduced size can induce magnetism. It was indeed exciting when we discovered that an icosahedric Rh_{13} cluster is ordered ferromagnetically. This prediction was promptly tested experimentally by Bloomfield et. al.,¹² who not only found Rh_{13} to be ferromagnetic in agreement with our prediction, but also found a strong dependence of magnetic moment on cluster size. This will be discussed in greater detail in section III.

Using the Monte Carlo method we studied the temperature and magnetic field dependence of antiferromagnetically coupled Ising clusters.⁶ We showed that the variation of magnetization with applied field and temperature depends upon the geometry of the clusters: icosahedral clusters behaved as frustrated paramagnets while cuboctahedric clusters exhibited well-defined ground states. The results explain the experimental data on Cr_n clusters.¹⁶

The effect of local symmetry on the magnetic moment at the Mn sites in Mn_xAl_{1-x} quasicrystals has been investigated⁸ by modeling the quasicrystals by clusters. Our studies, having a central Mn surrounded by Al_n ($n \leq 54$) atoms in cuboctahedral and icosahedral arrangement show that the Mn sites do carry a magnetic moment at small cluster sizes. The moment is, however, quenched as the cluster size is increased irrespective of the geometry. This quenching is shown to be a direct consequence of the mixing between the Mn d states and the Al p states in these geometries. The existing theoretical picture,¹⁷ which is based on calculations on smaller clusters and predicts that the magnetic Mn sites in MnAl quasicrystals are a result of icosahedral symmetry, was shown to be incorrect. Our results account for the experimental data.¹⁸

The magnetic coupling between Fe layers, separated by spacer layers consisting of up to two atomic planes of 3d transition metal elements (Sc, Ti, V, Cr, Fe, Co, Ni and Cu), has been studied¹⁰

systematically by using two complimentary theories based on cluster and band structure methods. The Fe layers are found to be ferromagnetically coupled in all cases except for Cr where this coupling alternates from ferro- to anti-ferromagnetic depending on whether the spacer layers are odd or even. Furthermore, the spacer layers involving Sc, Ti, and V are anti-ferromagnetically coupled to Fe, while Co and Ni layers are coupled ferromagnetically. Experimental verification of some of these predictions are eagerly awaited.

(ii) Clusters as Super-atoms

The idea that clusters can be treated as super-atoms originated from the pioneering work of Knight et. al.,¹⁹ who demonstrated that Na clusters with 2, 8, 20, 40, ... atoms exhibited unusual stability. They showed that such stability originated from the electronic shell closure. Later experiments^{20,21} demonstrated that the clusters with closed electronic shells are also chemically inert and analogous to the rare gas atoms. For very large clusters, Martin et. al.²² observed that clusters with closed atomic shells also exhibit unusual stability. We combined these two stability requirements²³ and proceeded to design a compound cluster that had both electronic and atomic shells closed. For example, Al_{12}C , having an icosahedric structure satisfies both of the above criteria. Indeed, we found this cluster to be an unusually stable compound compared to Al_{13} .

We then explored²⁴ the chemistry of Al_{12}C and Al_{13} clusters. Al_{12}C , with 40 valence electrons, has closed electronic shells and should mimic the chemistry of rare gas atoms. On the other hand, Al_{13} , with a hole in the outer electronic shell, should be quite reactive. We studied the interaction of Al_{12}C and Al_{13} with hydrogen by calculating the energetics of reaction. We found that Al_{12}C is unreactive towards hydrogen, while Al_{13} is quite reactive.

This study was taken a step further²⁵ to demonstrate that the chemistry of Al_{13} should be like that of a Cl atom. Indeed, the calculations revealed that the electron affinity of Al_{13} is almost identical with that of Cl. The study of the interaction of Al_{13} with a K atom revealed that they are strongly bonded by an ionic interaction similar to that in KCl. The fact that the chemistry of atoms can be changed by going into clusters can be important to materials science, as novel materials with clusters as building blocks of matter can be envisioned. We discuss this possibility in more detail in the next section.

(iii) Hydrogen Uptake by a Metal Ion

Quantum-chemical calculations including correlations have been carried out²⁶ to study the amount and nature of hydrogen uptake by a Li atom in neutral as well as in ionic form. We have found that while the neutral Li atom cannot bind more than one hydrogen atom

the cation can bind a large number of hydrogen atoms in molecular form. This contrasting behavior originates from the fact that the bonding of hydrogen with neutral Li is covalent while that with the cation is primarily caused by polarization. The bonding of hydrogen with the Li^- anion exhibits dual nature. The first H_2 molecule binds to the anion dissociatively while the subsequent H_2 molecule can only exist in a physisorbed state.

The electronic structure and the stability of cationic, neutral, and anionic NiH_n ($n=1,2,4$, and 6) clusters were also studied.²⁷ While the cations are found to bind hydrogen in molecular form, neutral and anionic clusters have dissociated hydrogen at small sizes. NiH_4^{++} and NiH_4^{--} are shown to be stable despite Coulomb repulsion between the extra charges.

Our prediction²⁸ that up to seven H_2 molecules can be trapped to one Ni^+ ion was later verified experimentally.²⁹ We have also demonstrated that the large surface-to-volume ratio in small metal clusters as well as their unique individual geometries can have significant effect on their reactivity with gas molecules. This work may have relevance to the study of heterogeneous catalysis as well as hydrogen storage.

(iv) Metallo-Carbohedrenes

Recently Castleman and co-workers observed³⁰ an unusually stable cage-like network consisting of eight Ti and twelve carbon atoms (Ti_8C_{12}). These clusters, known as metallo-carbohedrenes or "met-cars" are fundamentally different from the fullerenes. The presence of metal atoms affects the nature of bonding in the met-cars, as well as their electronic, magnetic, and optical properties. Since many transition metal-carbon clusters form the met-car structure. It is likely that these clusters can be assembled to form cluster materials analogous to fullerene-based materials.^{31,32}

We carried out the first theoretical study⁵ of the structure and stability of the met-car. Our work revealed two important features: there is a strong C-C and metal-carbon bonding and the geometry of the met-car is a distorted dodecahedron. There is significant delocalization of electrons characteristic of the metallic systems. Numerous theoretical studies³³ have been carried out in these systems since our work, and these results are in general agreement with our work.

In the bulk phase, Ti and C form a very stable carbide with a NaCl structure. In contrast to met-cars, the bulk phase has no C-C bonds and is stabilized by Ti-C bonds alone. We studied the stability of the cubic fragments of the bulk and found them to have binding energies comparable to met-cars. By studying smaller prototype Ti_nC_m clusters, we showed³⁴ that the met-cars and the cubic structures are two different families whose formation is governed

by relative abundance of Ti and C. The Ti rich environment favors the NaCl structure while the C rich environment favors met-car structures. These findings are supported by recent experiments.³⁵

(v) Optical Properties of Mixed Clusters

The ground state properties of simple metal clusters can, in large part, be explained by electronic shell structure effects. The optical response, on the other hand, depends upon the energy differences between occupied and unoccupied electronic orbitals. We showed³⁶⁻³⁸ that selective changes in the position of single-particle levels can be induced by changing the chemical composition of the clusters. With respect to pure clusters, the impurity in bimetallic clusters like MgK_x and NaK_x was found to induce unequal shifts in the single particle levels. These shifts were reflected in a conspicuous way in concerted variations of both the ground state properties and the optical properties. The calculations were carried out for the first time using the two-step jellium model as well as the ab initio molecular orbital theory. Our studies not only helped to explain some of the experimental data³⁹ but also illustrated a rich variety of problems that can be studied in mixed clusters.

(vi) Stability and Fragmentation of Multiply Charged Clusters

A number of years ago, we were the first ones^{40,41} to theoretically study the stability and fragmentation pattern of multiply charged clusters. We had predicted⁴⁰ that one of the likely fragments in the Coulomb explosion of doubly charged clusters is a magic number cluster (cluster with closed electronic shells). This prediction has since been verified both experimentally⁴² and theoretically using molecular dynamics simulation.⁴³ The later calculation also revealed that Na_{10}^{++} preferred to fragment into Na_7^+ and Na_3^+ and not into Na_9^+ and Na^+ , even though Na_9^+ is a magic cluster like Na_3^+ . We were able to provide⁴⁴ an explanation of this result. We showed that the channel $Na_{10}^{++} \rightarrow Na_7^+ + Na_3^+$ was preferred, since Na_7^+ can undergo Jahn-Teller distortion to further lower its energy, while Na_9^+ cannot. We systematically⁴⁵ studied the fragmentation of Mg_n^{++} clusters and showed that the transition from metastability to stability can occur in Mg_n^{++} as a function of size, and that the presence of barriers against fission can make even a doubly charged dimer stable. These predictions are continually witnessing experimental verification.

(vii) Cluster-Support Interaction

The study of supported metal clusters is becoming increasingly important, as it has become experimentally feasible to deposit mass-selected clusters⁴⁶ on various substrates. Furthermore, an understanding of cluster-support interaction is necessary to pave the way for using clusters in technological applications. In the

initial phases the clusters are expected to grow in two dimensions on a substrate. How does the stability of clusters in two dimensions differ from that in free space? We were the first theoretical group to tackle this problem. Our ab initio molecular orbital calculations⁴⁷ of Al_n and Li_n clusters grown in two dimensions with different crystallographic orientations revealed a nonmonotonic dependence of the binding energies on cluster size with conspicuous maxima corresponding to close atomic packing. Unlike in free-space clusters, the atomic packing becomes a dominant feature for two-dimensional cluster growth from the beginning. The results agree with recent experimental findings.⁴⁸

We also studied the effect of temperature⁴⁹ on the structural integrity of a 55-atom Be cluster in free space as well as when supported on a metal surface. The melting point of the free cluster was found to be significantly lower than that of the bulk. We showed that the interaction of the surface with the cluster can complicate the conventional interpretation⁵⁰ of the melting point. Our work provided a cautionary remark that the melting point of a supported cluster determined from its change of shape, as is done traditionally, can provide misleading information.

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B. Publications (current funding cycle - 1992 to present)

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C. Professional Activities

Invitations to speak at Conferences

P. Jena

International Conference on "Clusters and Fullerenes", Trieste 1992	Italy	
American Chemical Society meeting, Washington D.C.	U.S.A.	1992
IX-NACMP Meeting, Bombay (declined) 1992	India	
International Symposium on "Local Order in Condensed Matter Physics", Jekyll Island	U.S.A.	1993
International Workshop on Ultrafine Particles and Nanostructured Materials, Stockholm	Sweden	1993
NATO Advanced Study Institute on Nanophase Materials, Corfu	Greece	1993
International Symposium on Atomic and Nucleonic Clusters, Santorini 1993	Greece	
3rd International Summer School, Jyvaskyla (a series of 10 lectures on clusters)	Finland	1993
International Union of Materials Research Society Meeting, Tokyo 1993	Japan	
International Conference on Hydrogen in Metals, Yalta (declined) 1993	Ukraine	
International Conference on Current Trends in Physics, Bombay (declined) 1993	India	
International Conference on Nanophase		

Materials, Davos	Switzerland	
1994		
March Meeting of the American Physical Society, Pittsburgh	U.S.A.	1994
First Russian Conference on Clusters, St. Petersburg (declined)	Russia	
1994		
VII International Symposium on Small and Inorganic Clusters, Kobe	Japan	
1994		

♦ Fifteen seminars/colloquia given in seven countries since 1992.

S. N. Khanna

International Symposium on Small Particles and Inorganic Clusters, Chicago, Illinois, 1992.

First International Conference on the Theory of Atomic and Molecular Clusters, Leer, Oldenberg, Germany, 1993.

International Symposium on Local Order in Condensed Matter Physics, Jekyll Island, U.S.A., 1993.

Symposium on the "Physics of Clusters" at the Southeastern American Physical Society Meeting in Columbia, South Carolina, 1993.

March Meeting of the American Physical Society at Pittsburgh, 1994.

77th Canadian Chemical Society Conference, Winnipeg, Canada, 1994.

♦ Six seminars/colloquia in four countries.

B. K. Rao

International Symposium on molecules to materials, Bhubaneswar, India, 1992.

Gordon Research Conference on hydrogen-metal systems, 1993.

Third Interrepublic conference on hydrogen material science and chemistry of metal hydrides, Kiev, Ukraine, 1993, (declined).

Conference on current trends in atomic and molecular physics, Bombay, India, 1993.

First Russian Conference on Cluster Chemistry, St. Petersburg, Russia, 1994.

Conference on "Solid State Physics: Fundamentals and Applications," Alushta, Ukraine, 1994.

- ◆ Five seminars/colloquia in three countries.

Conferences Organized

Workshop on "Regional Center for Studies of Finite Systems," Richmond, October 1992.

International Conference on "Local Order in Condensed Matter Physics," Jekyll Island, 1993.

Gordon Research Conference on "Hydrogen-Metal Systems," Tilton, N.H. 1993.

Symposium on Atomic Clusters, American Physical Society, Southeastern section, Columbia, SC, 1993.

Focused Sessions on Clusters and Cluster-Assembled Materials, March Meeting of the American Physical Society, Pittsburgh, PA.

Symposium on Clusters and Cluster Materials, APS March Meeting, Pittsburgh, PA, 1994.

International Workshop on Clusters and Nanostructured Materials, Bhubaneswar, India, 1994.

D. Degrees earned by students

Scott Weber, M.S.
Budda Reddy, M.S.
Jiangang Niu, M.S.
Budda Reddy, Ph.D, 1994
Jiangang Niu, Ph.D, 1995.

E. Personnel Supported

J. P. Julien (Visitor)
F. Reuse (Visitor)
B. Waestberg (Postdoctoral Fellow)
H. Zheng (Postdoctoral Fellow)
S. Weber (Graduate Student)
J. Niu (Graduate Student)
B. Reddy (Graduate Student)
P. Jena (Summer)
S. N. Khanna (Summer)
B. K. Rao (Summer)